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ORGANOMETALLIC POLYMERS AS PRECURSORS TO CERAMIC
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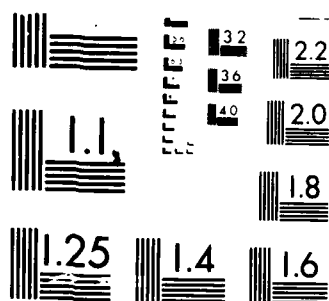
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R. Laine, Y. Blum, R. Hamlin, A. Chow

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We have found that a large variety of homogeneous and heterogeneous catalysts will promote the formation of silicon-nitrogen bonds via a dehydrocoupling coupling reaction of Si-H bonds with N-H bonds. This reaction can be used to synthesize a wide variety of tractable oligo- and polysilazanes. The molecular weight, the viscoelastic properties and the linearity of the polymer can be controlled through proper choice of catalyst and reaction conditions. In addition, the catalyst promotes polymer crosslinking during pyrolysis which leads to high ceramic yields and silicon nitride purities > 95%.

Nitrogen

hydrogen

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22a NAME OF RESPONSIBLE INDIVIDUAL

Kenneth Wynne

22b TELEPHONE (Include Area Code)

(202) 696-4410

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ORGANOMETALLIC POLYMERS AS PRECURSORS TO CERAMIC MATERIALS:
NITRIDE AND SILICON OXYNITRIDE

Richard M. Laine, Yigal D. Blum
Richard D. Hamlin, and Andrea Chow
Inorganic and Organometallic Chemistry,
Physical Polymer Chemistry Program and
the Ceramics Program
SRI International, Menlo Park, CA 94025

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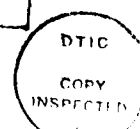
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NITRIDE AND SILICON OXYNITRIDE

Richard M. Laine*, Yigal D. Blum, Richard D. Hamlin, Andrea Chow,
Contribution from Inorganic and Organometallic Chemistry, Physical
Polymer Chemistry Program and the Ceramics Program, SRI
International, Menlo Park, CA 94025

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Introduction:

The general industrial approach to the fabrication of ceramic materials relies, to a great extent, on processing techniques wherein blended mixtures of simple, sometimes ill-defined (in a chemical sense), inorganic materials are shaped and then heated at high temperature to obtain a finished ceramic product. In the past, process optimization commonly meant optimizing each process step empirically rather than through the use of scientific fundamentals. As a result, the discovery of new ceramic materials or new processing techniques were rare and progress was made only by pursuing analogies to known processes.

In the last three decades, changes in technology have created a need for new, stronger, more stable structural (advanced) ceramics to meet new operating tolerance requirements, particularly in aerospace applications. This need has spurred the search for ceramics that fulfill these new tolerance requirements and for alternate, potentially more facile methods of preparing ceramic materials in general.

One very novel approach to ceramics preparation, first proposed more than 20 years ago by Chantrell and Popper¹ and recently refined by Wynne and Rice², is to synthesize inorganic or organometallic polymer precursors to ceramics. If the physical properties of these precursors are analogous to those of simple organic polymers, then one can shape them at low temperatures using processing techniques developed for organic polymers and then heat the formed polymer to transform it to the finished ceramic shape.

In theory, the concept offers a variety of exceptional advantages over current processing techniques including savings on energy and capital

equipment costs; and, close control of product stoichiometries, purities and morphologies. On a practical level, because we must learn how to design and synthesize precursors, and then pyrolyze them, the opportunity exists to identify and delineate the general criteria required to prepare all types of materials. We have recently proposed³⁻⁵ a set of general design criteria for the synthesis of inorganic and/or organometallic precursors to refractory metals and ceramic materials. These criteria are best summarized as follows:

Given the empirical formula of a particular ceramic material, it should be possible to synthesize a chemical compound, a monomer, that closely approximates that empirical formula. This monomer then represents a potential precursor to the desired ceramic material. If the monomer can be successfully transformed into a tractable polymer that can be shaped and then made infusible, it will be a useful ceramic precursor.

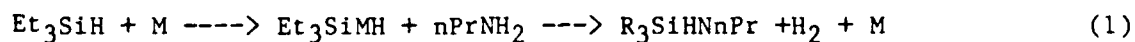
It is important to note that a great many variables come into play in the synthesis and pyrolytic conversion of preceramic materials into finished products. Some design criteria are specific to the type of precursor polymer and ceramic material desired. For example, in the synthesis of silicon nitride precursors, the precursor may contain excess silicon because finely divided silicon will react with N_2 to form Si_3N_4 during the pyrolysis step. The delineation of most of these variables remains to be done before soundly based scientific principles can be established. The work presented here represents our continuing efforts to develop new, improved synthetic routes to ceramic precursors of Si_3N_4 and Si_2ON_2 , and to validate or refine initially proposed design criteria.³⁻⁵

Synthesis and Pyrolysis of Polysilazanes

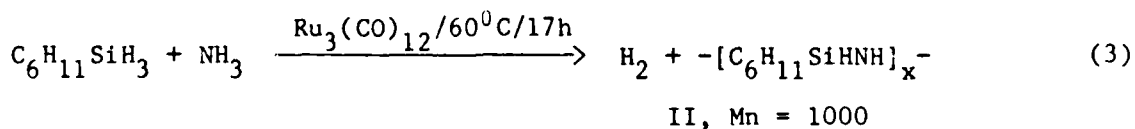
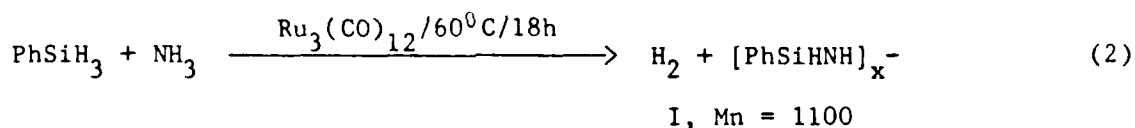
Historically, interest in the synthesis of linear polysilazanes and polydimethylsilazane, $-\text{[Me}_2\text{SiNH]}_x-$ in particular, derives from the fact that it is the nitrogen analog of polydimethylsiloxane, $-\text{[Me}_2\text{SiO]}_x-$, of commercial importance in silicone oils, rubbers etc. Given that $-\text{[Me}_2\text{SiNH]}_x-$ has one more functional position (the N-H) than $-\text{[Me}_2\text{SiO]}_x-$, the number of potential polymer derivatives should be that much greater. Surprisingly, no one has succeeded in making linear polydimethylsilazanes with molecular weights greater than ca. 1,200 daltons and crosslinked polysilazanes with molecular weights of greater than 15,000 daltons, even though polydimethylsiloxanes with molecular weights greater than 1M daltons are common. To date, no one has provided a reasonable explanation for this gross disparity.

Despite this obvious problem, a number of research groups have attempted to validate the Chantrell and Popper concept of preceramic polymers through efforts to synthesize precursors to silicon carbide (SiC) and silicon nitride (Si_3N_4).⁶⁻¹⁰ These efforts have met with limited success; perhaps, because of the very immature state of this multidisciplinary science. One silicon carbide based ceramic fiber, Nicalon, prepared using a preceramic polycarbosilane⁶ (molecular weight ca. 2000 daltons), is now available commercially. However, continued efforts to refine the precursor synthesis process are likely to lead to improvements that will permit the commercialization of other ceramic products based on the use of preceramic polymers.

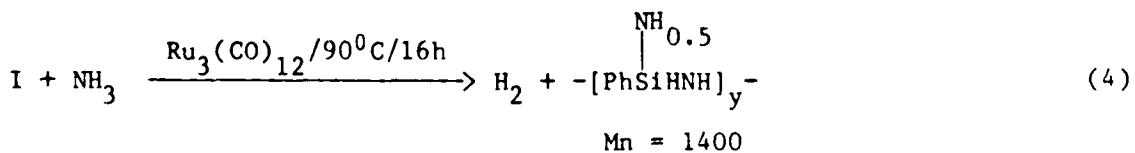
Our own efforts in this area¹¹⁻¹⁴ have focussed on the design and catalytic synthesis of precursors to silicon nitride, silicon oxynitride (Si_2ON_2) and recently boron nitride¹⁵ for use in coating, binder and fiber applications. Our approach to the synthesis of Si_3N_4 and Si_2ON_2 preceramics relies on the use of a catalytic reaction wherein a transition metal (M) activates an Si-H bond in a hydrosilane.¹² The activated complex can then react with ammonia or an amine to form an Si-N bond with release of H_2 as illustrated in Reaction (1). The process of dehydrocoupling, Reaction (1),

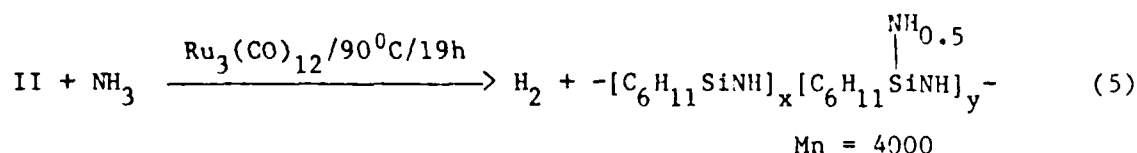


can be used to form linear oligo- and polysilazanes as illustrated in the reactions of either phenyl or n-hexylsilane with NH_3 at 60°C :¹⁶



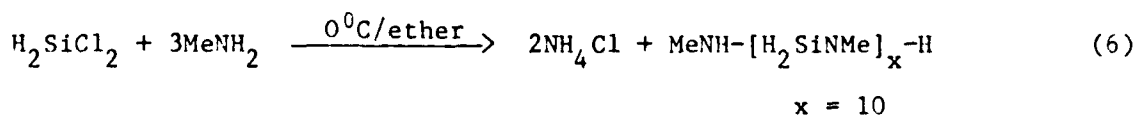
When the products of reactions (2) and (3) are heated at 90°C with additional NH_3 , oligomers I and II crosslink but only via -NH- bridges to give tractable polymers:





Because we can obtain crosslinking at higher temperatures, these polymer/catalyst systems provide the latent reactivity² required to thermoset the polymer making it infusible. The ceramic yields for pyrolysis of these polymers are 70% and 36%. The ceramic products are Si_3N_4 and carbon. For the phenyl polymer produced in reaction (4) the carbon content is 2% and for the hexyl polymer produced in reaction (5) the carbon content is 9%. X-ray powder patterns of either ceramic product sintered at 1600°C (under 1 atm of N_2 for 16-20h) reveal the presence of Si_3N_4 alone, without any evidence of SiC .

In order to increase the ceramic yields and reduce the carbon content of the ceramic products, it was necessary to switch to another type of precursor containing much less carbon. Seyferth et al¹⁰ described a preliminary study of the pyrolysis of $\text{MeNH}-(\text{H}_2\text{SiNMe})_x-\text{H}$, prepared as in reaction (6),^{10,17} wherein they were unable to detect the presence of carbon in the ceramic product.



The theoretical ceramic yield from $\text{MeNH}-(\text{H}_2\text{SiNMe})_x-\text{H}$ could be as high as 70.7% assuming complete loss of methyl groups and hydrogen. Given that the silicon to nitrogen ratio in the polymer is 1:1 and in silicon nitride it is 3:4, pyrolysis of $\text{MeNH}-(\text{H}_2\text{SiNMe})_x-\text{H}$ in the absence of N_2 will produce a 15% excess of silicon. Under the conditions of

pyrolysis this silicon can react with N_2 . Consequently, pyrolysis under N_2 could increase the theoretical yield to 78.4% and the product would be Si_3N_4 , again assuming complete loss of methyl groups and hydrogen.

Unfortunately, Seyferth et al¹⁰ reported that pyrolysis of oligomers of $MeNH-[H_2SiNMe]_x-H$ ($x = 10$) gives ceramic yields of only 39%. We have repeated this work and find that the low ceramic yields derive in part from the low molecular weights of the precursor oligomers. In addition, we find that the ceramic product is always contaminated with 15-20% carbon (vide infra).

As a result of the above dehydrocoupling polymerization studies, we recognized that $MeNH$ caps in $MeNH-[H_2SiNMe]_x-H$ were potentially available for dehydrocoupling with the H_2Si moieties of the polymer to promote the formation of higher molecular weight species and coincidentally increase the ceramic yields. In order to explore the utility of the $MeNH-[H_2SiNMe]_x-H$ oligomers as precursors to silicon nitride, we synthesized the precursor according to reaction (6) and examined the effects of catalytic modification as shown in (7).

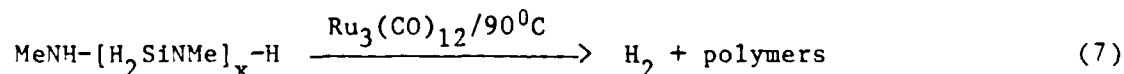
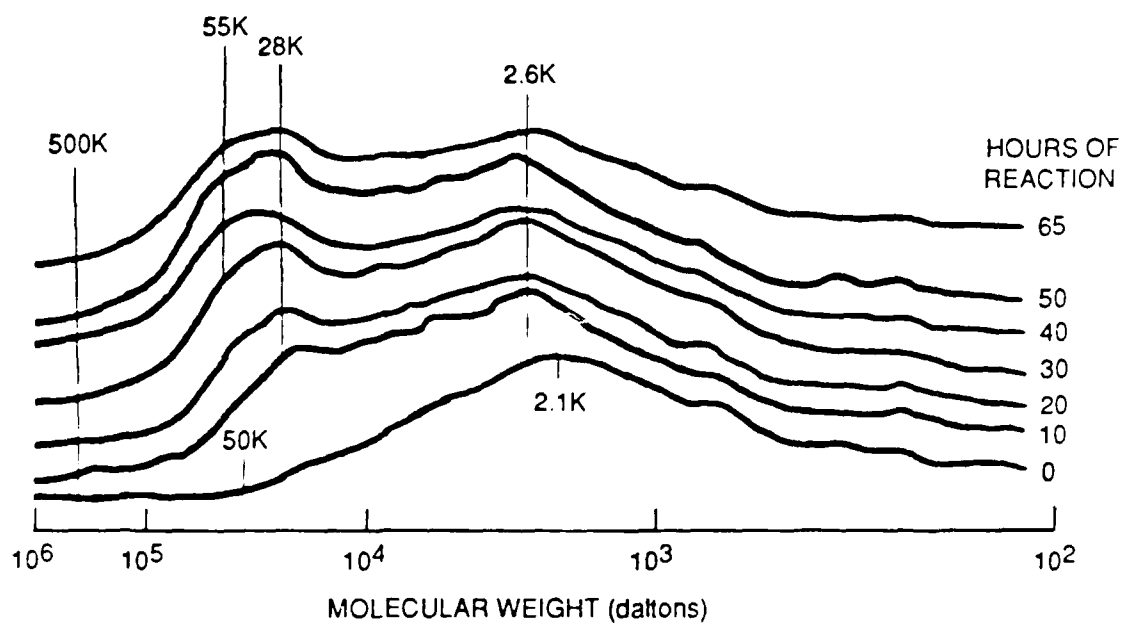


Figure 1 illustrates the changes in molecular weight that occur with time in reaction (7). One important feature of the results shown in Figure 1 is that a reasonable proportion of the products observed after 65 h of reaction have molecular weights in excess of 50K daltons and in some instances over 500K.¹⁶ Until now no one has succeeded in making polysilazanes with this molecular weight.

INSERT FIGURE 1



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FIGURE 1 GPC RESULTS OF $[H_2SiMe]_x$ POLYMERIZATION CATALYZED BY $Ru_3(CO)_{12}$

Table 1 briefly presents the results of pyrolysis studies directed towards identifying the effects of precursor molecular weight and viscosity on ceramic yields and selectivities.¹⁸ The important findings of these studies are: (1) The molecular weight of the precursor itself plays a role in the total ceramic yield; (2) Catalytic chain extension or crosslinking can be used to increase the overall ceramic yield and modify the viscoelastic properties of the precursor polymer; and, (3) Silicon nitride purity is determined by the precursor itself and is independent of its molecular weight and viscoelastic properties.

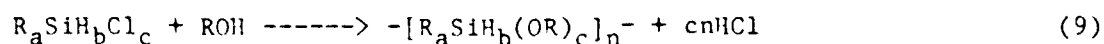
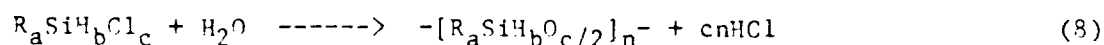
Oligomer	Mn (GPC)	Viscosity (poise)	Ceramic Yield (% at 900°C)	% Si ₃ N ₄
-[H ₂ SiNMe] _x - x = 10	600-700	1	40	80-85
-[H ₂ SiNMe] _x - x = 19	1150	5	45-50	80-85
-[H ₂ SiNMe] _x - Ru ₃ (CO) ₁₂ /90°C/THF for 30h	2100	18	60-65	80-85
-[H ₂ SiNMe] _x - Ru ₃ (CO) ₁₂ /90°C/THF for 65h	2500	100	65-70	80-85

Table 1. Pyrolysis Studies on MeNH-[H₂SiNMe]_x-H Oligomers and Polymers

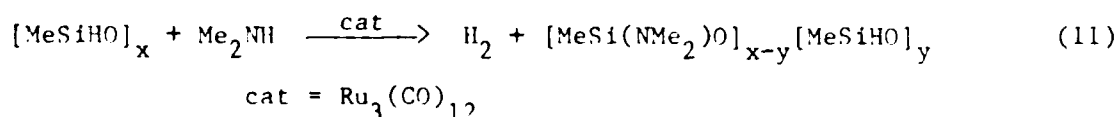
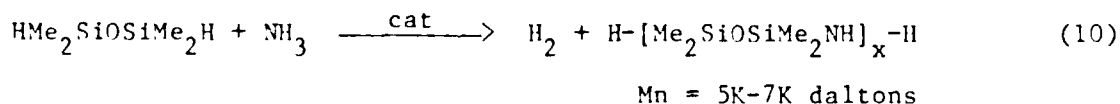
The products themselves are amorphous black glasses that fracture conchoidally. Carbon is the major impurity found in all the ceramic products in Table 2. Carbon content regularly accounts for 15-18% of the ceramic product. Oxygen content is normally 0.5-2.0% mainly as a result of the sensitivity of the polymers to moisture. Heating the black glass at higher temperatures (1650-1725°C under N₂) normally results in a 10-20% decrease in ceramic yields and the appearance (by X-ray powder diffractometry) of α and some β silicon nitride.

Synthesis and Pyrolysis of Polysiloxazanes

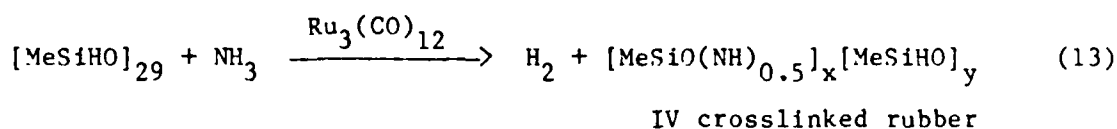
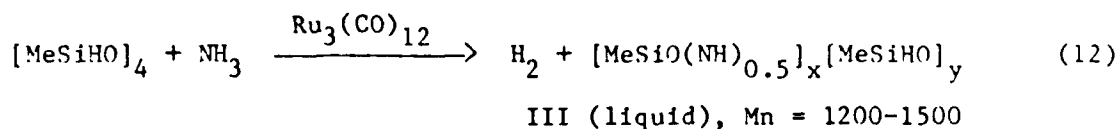
In a similar manner, we have attempted to make polymer precursors to Si₂ON₂, using as precursors available commercially. The commercial precursors are prepared by hydrolysis or/and alcoholysis of chlorosilanes:



Dehydrocoupling the Si-H bonds with ammonia or amines provides polysiloxazanes as illustrated by reactions (10) and (11):¹⁶



Polysiloxazane precursors to Si_2ON_2 can be prepared as shown in reactions (12) and (13):



The rheological properties of III and IV are highly dependent on reaction conditions.¹⁶ To our knowledge, the polysiloxazanes produced in reactions (11)-(13) represent a new family of polymers without precedent in the literature.

Pyrolysis of either material provides similar results. Table 2 shows data obtained for pyrolysis of IV.¹⁸ X-ray powder patterns of the product heated at 1600°C reveal the presence of Si_2ON_2 but no Si_3N_4 or SiC ; although these materials and carbon may be present in amorphous form.

Pyrolysis Temp ($^\circ\text{C}$)	Atm	Ceramic Yield (%)	Analysis (wt %)					X-ray ^a
			Si	N	O	C	H	
800	N_2	75	42.5	5.0	27.8	13.7	0.8	--
1600	N_2	64	49.8	8.5	30	11.7	0.1	Si_2ON_2
800	NH_3	88	48.3	21.0	28.4	1.8	0.5	--
1600	NH_3	78	55.9	b	b	0.4	0.1	Si_2ON_2

Table 2. Pyrolysis of $[\text{MeSiO}(\text{NH})_{0.5}]_x [\text{MeSiHO}]_y$ under various conditions. a. X-ray powder patterns found. b. Insufficient combustion

Concluding Remarks

These studies add to the growing evidence supporting the viability of the Chantrell-Popper concept of preceramic polymers. We have demonstrated the feasibility of synthesizing tractable, moderate molecular weight polymers which can be rendered infusible by higher temperature crosslinking. Pyrolysis of these polymers provides high ceramic yields with good selectivity to silicon nitride and silicon oxynitride. Moreover, we have now demonstrated the utility of these polymers for use in binder and coating applications.

In general the catalytic dehydrocoupling approach to the synthesis of polysilazanes and polysiloxazanes is at an early stage. Many features of the process are poorly defined and others unknown. Current objectives in these laboratories are directed towards reducing the carbon content in the silicon nitride and silicon oxynitride products by examining the effects of pyrolysis in NH_3 rather than N_2 . Additional efforts are centered on the use of dehydrocoupling as a catalytic route to polymer precursors to boron nitride, BN, and a variety of ceramic alloys.

Acknowledgements

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